

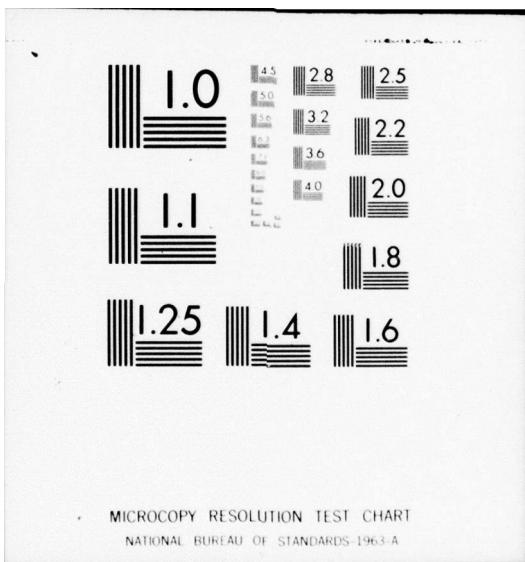
AD-A040 126 UTAH UNIV SALT LAKE CITY DEPT OF CHEMISTRY  
RATES OF RAPID CHEMICAL REACTIONS. (U)  
MAR 77 E M EYRING

F/G 11/3

UNCLASSIFIED

AF-AFOSR-2444-73  
AFOSR-TR-77-0649 NL





MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

**ADA040126**

AFOSR - TR - 77 - 0649

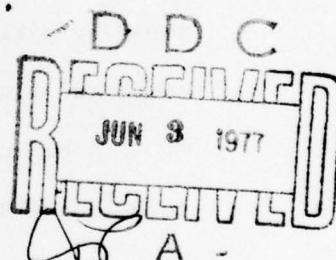
March 28, 1977

12

see 1473  
in back

FINAL TECHNICAL REPORT TO THE  
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH,  
CHEMICAL DIRECTORATE

Approved for public release  
distribution unlimited.



Project Title: RATES OF RAPID CHEMICAL REACTIONS  
Institution: University of Utah, Salt Lake City, Utah  
Principal Investigator: Dr. Edward M. Eyring  
Grant Award Number: AFOSR 73-2444  
Report Period: December 1, 1972 to January 31, 1977

COPY

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)  
NOTICE OF TRANSMITTAL TO DDC  
This technical report has been reviewed and is  
approved for public release IAW AFR 190-12 (7b).  
Distribution is unlimited.

A. D. BLOSE  
Technical Information Officer

OK OA  
305

SUMMARY

A nanosecond time scale laser flash photolytic study of the kinetic behavior of carbocyanine dyes in low temperature glasses was completed and published. So also was an ultrasonic absorption kinetic investigation of the complexation of aqueous silver (I) ion by thiosulfate ion. This latter work led into a large number of ultrasonic kinetic studies of metal ion complexation in solution by a variety of anionic and neutral ligands. In the case of crown ether ligands, such as 18-crown-6 and 15-crown-5, observed rates were surprisingly far below diffusion control and were influenced instead by cation desolvation kinetics and conformational changes in the uncomplexed ligand.

A minicomputerization of the laser Debye-Sears ultrasonic absorption technique played an especially important role in these successful complexation kinetic experiments. This very productive minicomputerization led us to automate a spectrophotometric electric field jump relaxation method experiment, a task completed just after the expiration of the grant.

A thorough study of the thermal degradation of a polyperfluoroalkyl ether in the presence of iron and titanium metal coupons was carried out by a variety of experimental techniques. Results obtained, particularly by thermogravimetric and gas chromatographic mass spectral analytical methods, indicated a free radical mechanism consistent with the conclusions of earlier workers.

The elucidation of the rate and mechanism of formation of titanium fluorides on the surface of titanium metal coupons bathed in hot polyperfluoroalkyl ether lubricant was set as a goal late in the four year grant

period. An adaptation of photoacoustic spectroscopy (PAS) incorporating a piezoelectric transducer instead of a microphone was selected for this task. The feasibility of making optical absorbance measurements of an opaque surface at high chopping frequencies (up to ~250 KHz) of the incident light has been demonstrated. The use of this technique in measuring short fluorescence lifetimes in opaque materials has also been demonstrated by PAS signal phase angle measurements in ND:laser glass as well as in solid Nd<sub>2</sub>O<sub>3</sub>.

ACCESSION NO.	White Section	<input checked="" type="checkbox"/>
NTIS	Buff Section	<input type="checkbox"/>
DDC		
UNANNOUNCED		
JUSTIFICATION		
BY.....		
DISTRIBUTION, AVAILABILITY CODES		
DIST.	AVAIL.	REQ. OF SPECIAL
A		

DISCUSSION

The goals set at the inception of this four year grant were inspired by practical silver halide photographic emulsion problems. During the grant period two scientific papers were published that were anticipated by the original research proposal: Paper (9) in the attached list of publications dealt with a pulsed laser flash spectroscopic study of carbocyanine dyes used as sensitizers in photographic emulsions. Paper (15) reported the very rapid kinetics of complexation of aqueous silver(I) ion by thiosulfate ion, a classic reaction for "fixing" photographic negatives. The flash calorimetric technique that was originally proposed for the dye sensitizer studies turned out to have an unsuitably slow response time, but the familiarity gained with this technique has since proven very valuable in our development of a novel photoacoustic spectroscopy technique for investigating solid surfaces described below. The ultrasonic absorption technique that we foresaw using to measure silver ion complexation kinetics has since turned out to be the most productive research tool in our laboratory. References (12), (15), (16), (18), (19), and a half dozen other manuscripts in preparation and in press were made possible by the minicomputerized Debye-Sears Ultrasonic absorption spectrometer envisioned in our 1972 proposal.

A partial shift in emphasis away from photographic chemical problems and toward corrosion related phenomena appears in the proposal for the period August 1, 1973 to July 31, 1974. An electric field jump kinetic study of the hydrolysis of iron (III) was planned for spectrophotometric

execution at an ultraviolet wavelength. Several electric field jump relaxation method kinetic studies [(4), (5), (6) and (14)] were completed during this grant year, but the sensitivity of the method was not sufficient to detect the small ultraviolet absorbance amplitude change associated with the fast transient of iron(III) hydrolysis.

The proposal for the year August 1, 1974 to July 31, 1975 focused on kinetic studies of metal ion complexation ( $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$ ) by ultrasonic absorption spectroscopy, electric field jump relaxation method kinetic studies of aqueous protolytic reactions, and further fluorescence studies of cyanine dyes. Resulting ultrasonic studies of complexation of monovalent and divalent cations by various crown ethers and cyclodextrins have been extraordinarily fruitful. In addition to paper (18) the following manuscripts acknowledging AFOSR support are at the various stages of the publication process indicated for each: 1) G. W. Liesegang, M. M. Farrow, F. A. Vazquez, N. Purdie, and E. M. Eyring, "Ultrasonic Absorption Kinetic Studies of the Complexation of Aqueous  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Rb}^+$ ,  $\text{Tl}^+$ ,  $\text{Ag}^+$ ,  $\text{NH}_4^+$ , and  $\text{Ca}^{2+}$  by 18-Crown-6," J. Amer. Chem. Soc., in press for August, 1977; 2) R. P. Rohrbach, L. J. Rodriguez, E. M. Eyring, and J. F. Wojcik, "An Equilibrium and Kinetic Investigation of Salt-Cycloamylose Complexes," J. Phys. Chem. in press for May, 1977; 3) G. W. Liesegang, M. M. Farrow, L. J. Rodriguez, E. M. Eyring, and N. Purdie, "Dynamics of Conformational Change in Aqueous 18-Crown-6 by an Ultrasonic Absorption Method," accepted for publication subject to minor revision by Int. J. Chem. Kinetics; 4) G. W. Liesegang and E. M. Eyring, "Kinetic Studies of Synthetic Multidentate Macrocyclic Compounds," in Synthetic Multidentate Macrocyclic Compounds,

R. M. Izatt et al., eds., Academic Press, N. Y., publication projected for Summer, 1977; 5) N. Purdie, E. M. Eyring, and L. J. Rodriquez, "Reaction Rate Measurements in Solution on Microsecond to Subnanosecond Time Scales," in Chemical Experimentation Under Extreme Conditions, B. W. Rossiter, ed., Interscience Publishers, N. Y., publication projected for Autumn, 1977; 6) L. J. Rodriquez, G. W. Liesegang, R. D. White, M. M. Farrow, N. Purdie, and E. M. Eyring, "Kinetic Studies of the Complexation of Monovalent Sodium, Potassium, Rubidium, Thallium and Silver Cations by Aqueous 15-Crown-5," to be submitted to *J. Phys. Chem.*; and 7) L. J. Rodriquez, G. W. Liesegang, M. M. Farrow, N. Purdie, and E. M. Eyring, "Kinetic Studies of Complexation of Divalent Strontium, Barium, Lead and Mercury Cations by Aqueous 15-Crown-5 and 18-Crown-6," manuscript in final stages of preparation.

The general thrust of these papers has been to demonstrate that crown ethers complex even the simplest cations at rates one to two orders of magnitude slower than diffusion control. The rate determining step in the ion complexation is instead first solvation sheath water loss from the cation. In some situations a conformational change of the crown ether ring also plays an important role in the complexation process. Cycloheptaamyllose (also called  $\beta$ -cyclodextrin) on the other hand complexes small anions such as  $\text{Cl}^-$  and  $\text{ClO}_4^-$  at rates that do not depend on desolvation rates but rather on simple steric factors. These results and their extrapolation to related systems are particularly interesting as a potential guide to the synthesis of homogeneous catalysts resembling those recently synthesized from crown ethers by Cram and coworkers at U.C.L.A.

With the exception of one study of the kinetics of a helix coil transition (17) the electric field jump apparatus has been a less productive research tool since August 1, 1974 than the Debye-Sears ultrasonic absorption spectrometer. This is a reflection of several factors: The spectrophotometric electric field jump technique is ill-suited to the study of reaction systems experiencing light absorbance changes outside the visible region of the electromagnetic spectrum. Protolytic reactions, particularly of visibly colored acids or bases in aqueous solution, are well enough understood at this point to warrant little further study. Until very recently (February, 1977) the complete mini-computerization of the electric field jump experiment had been delayed by a shortage of computer memory. There are some very interesting experiments in nonaqueous solvents that could be carried out productively with the now fully computerized electric field jump apparatus; however, the present emphasis of our AFOSR sponsored research lies in the unrelated field of photoacoustic spectroscopy of solid surfaces [see below].

The research proposal for the period August 1, 1975 to July 31, 1976 sketched plans for 1) a study of the mechanism of degradation of a poly-perfluoralkyl ether lubricant at elevated temperatures in the presence of various metals, 2) a kinetic study of aqueous titanium(III) hydrolysis, and 3) full automation of the ultrasonic absorption of electric field jump experiments. The first of these objectives was achieved in detail relying principally on mass spectrometric and thermogravimetric techniques rather than by  $^{13}\text{C}$  nmr and ultrasonic methods as originally proposed. A free

radical mechanism for the degradation of a polyperfluoroalkyl ether was confirmed and activation parameters for the thermal degradation were measured. Conclusions drawn from the date were similar to those of D. Sianesi, V. Zamboni, R. Fontanelli, and M. Binaghi, "Perfluoropolyethers: Their Physical Properties and Behaviour at High and Low Temperatures," *Wear*, 18, 85 (1971). Our work in this area is summarized in the first of two Appendices to this report.

Aqueous solutions of titanium(III) are so deeply colored when concentrated enough to cause significant ultrasonic absorption that they are too opaque to cw argon-ion laser light for Debye-Sears type ultrasonic absorption measurements to succeed. It may be possible to use the Dember effect [A. Bergman, C. R. Dickson, S. D. Lidofsky, and R. N. Zare, "Laser Generation of Transient Photocurrents in Liquids Without the Application of an Electric Field," *J. Chem. Phys.*, 65, 1186 (1976)] to make such a kinetic measurement. However, we plan to try a resonance type of ultrasonic absorption measurement (in the 0.5 to 10 MHZ ultrasonic frequency range) instead since optical transmission of the sample solution in this technique is irrelevant.

The total automation of our Debye-Sears ultrasonic absorption method has been reported (19). The more complex minicomputerization of the electric field jump relaxation method apparatus was finished just after the termination of this grant [February, 1977] and will be described in an as yet unwritten publication.

The last research proposal submitted was for the period August 1, 1976 to January 31, 1977. The principal theme was the development of a photo-

coustic spectrometer for identifying reaction products on the surface of metal coupons exposed to hot polyperfluoroalkyl ether lubricant.

This work has been eminently successful. A working photoacoustic spectrometer, using a piezoelectric transducer as the detector rather than the more conventional microphone, was reported at the 173rd American Chemical Society National Meeting in New Orleans on Tuesday, March 22, 1977 [M.M. Farrow, M. Auzanneau, R.K. Burnham, N. Purdie, and E.M. Eyring, "Photoacoustic Spectroscopy of Neodymium(III) Glass," Meeting Abstracts, Physical Chemistry Division, paper no. 113.] The novel aspect of this instrumentation is its capability of measuring rapid transient surface chemical phenomena over the entire 0 to 250 KHz frequency range with no apparent insuperable obstacles to attaining frequencies as high as 250 MHz. The highlights of this work are discussed in the second of two appendices to the present technical report.

Publications Acknowledging AFOSR Support Since December, 1, 1972

1. J. Lang, J. J. Auborn, and E. M. Eyring, "Kinetics of Octyl-phenyl Polyoxyethylene Alcohol Micelle Dissociation by a Stopped-Flow Technique," *J. Colloid Interface Sci.*, 41, 484 (1972).
2. R. C. Graham, G. H. Henderson, E. M. Eyring, and E. M. Woolley, "Molecular Associations in Non-Aqueous Solvents I. Thermodynamics of Dye-Dye Interactions in  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$ ," *J. Chem. Eng. Data*, 18, 277 (1973).
3. Z. A. Schelly, J. Lang, and E. M. Eyring, "Relaxation of Laser Induced Transient Plasmas in Liquids," *Monatshefte fuer Chemie*, 104, 1672 (1973).
4. D. J. Lentz, J. E. C. Hutchins, and E. M. Eyring, "Solvent Isotope Effects for Sulphonphthalein Indicator Dinanion-H<sup>+</sup> Recombination Kinetics," *J. Phys. Chem.*, 78, 1021 (1974).

5. S. L. Olsen, L. P. Holmes, and E. M. Eyring, "Pulsed Spectro-photometric Chemical Relaxation Measurements," *Rev. Sci. Instrum.*, 45, 859 (1974).
6. M. M. Farrow, N. Purdie, and E. M. Eyring, "Dissociation Field Effect Kinetic Study of Aqueous Samarium(III) Complexation by Murexide," *Inorg. Chem.*, 13, 2024 (1974).
7. R. C. Graham, G. H. Henderson, E. M. Eyring, and E. M. Woolley, "Molecular Associations in Nonaqueous Solvents II. Temperature Effects on Thermodynamics of Dye-Dye Interaction in  $C_6H_6$ ," *J. Chem. Eng. Data*, 19, 297 (1974).
8. J. T. Knudtson and E. M. Eyring, "Laser-Induced Chemical Reactions," *Ann Rev. Phys. Chem.*, 25, 255 (1974).
9. J. T. Knudtson and E. M. Eyring, "Photophysical Effects of Steroisomers in Thiacarbocyanine Dyes," *J. Phys. Chem.*, 78, 2355 (1974).
10. J. D. Owen, M. Steggall, and E. M. Eyring, "The Effect of Phloretin on Red Cell Nonelectrolyte Permeability," *J. Membrane Biol.*, 19, 79 (1974).
11. M. M. Farrow, N. Purdie, and E. M. Eyring, "The Kinetics of Complexation of Thallium(I) Triiodide in Aqueous Solution," *J. Amer. Chem. Soc.*, 97, 1968 (1975).
12. M. M. Farrow, N. Purdie, A. L. Cummings, W. Herrmann, Jr., and E. M. Eyring, "Kinetic Studies of Metal Ion Complexation and Dye Dimerization by Laser Ultrasound and Laser T-Jump," in *Chemical and Biological Applications of Relaxation Spectrometry*, E. Wyn-Jones, ed., D. Reidel Publishing Co., Dordrecht-Holland, 1975, pp. 69-83.
13. E. M. Eyring, "The Electric Field Jump Relaxation Method," *op. cit.*, pp. 85-90.
14. A. L. Cummings and E. M. Eyring, "Electric Field Jump Study of the Helix-Coil Transition of Aqueous Poly- $\alpha$ ,L-Glutamic Acid," *op. cit.*, 505-508.
15. M. M. Farrow, N. Purdie, and E. M. Eyring, "The Kinetics of Complexation of Silver(I) with Thiosulfate Ion in Aqueous Solution," *Inorg. Chem.*, 14, 1584 (1975).
16. M. M. Farrow, N. Purdie, and E. M. Eyring, "A Reevaluation of the Ultrasonic Absorption Spectra of Aqueous Samarium(III) Sulfate Solution," *J. Phys. Chem.*, 79, 1995 (1975).

17. A. L. Cummings and E. M. Eyring, "Helix-Coil Transition Kinetics in Aqueous Poly( $\alpha$ ,L-Glutamic Acid)," *Biopolymers*, 14, 2107 (1975).
18. G. W. Liesegang, M. M. Farrow, N. Purdie, and E. M. Eyring, "Ultrasonic Absorption Kinetic Studies of the Complexation of Aqueous Postassium and Cesium Ions by 18-Crown-6," *J. Amer. Chem. Soc.*, 98, 6905 (1976).
19. M. M. Farrow, S. L. Olsen, N. Purdie, and E. M. Eyring, "Automatic Ultrasonic Absorption Spectrometer," *Rev. Sci. Instrum.*, 47, 657 (1976).

APPENDIX I:

Description of Studies of the Thermal Degradation of  
a Polyperfluoroalkyl Ether Lubricant (DuPont PR-143)  
from the January 15, 1977 Interim Scientific Report  
for this grant.

C. E. Snyder, Jr. of Wright-Patterson AFB provided us with approximately two liters of DuPont PR-143. Depending upon the weight, this synthetic polyperfluoroalkyl ether can be used as a hydraulic fluid, gas turbine engine oil, or bearing grease. We have studied the degradation of the light engine lubricant under a variety of conditions. Our objective is to determine the reaction kinetics by which this lubricant degrades at high temperatures ( $\sim 550^{\circ}\text{F}$ ) in the presence and absence of gases and metals.

In subsequent experiments we degraded the lubricant thermally in the presence of titanium coupons following standard procedures.<sup>1</sup> Carbon-13 and fluorine-19 nmr spectra were obtained (on a Varian XL-100 spectrometer) on the distillate as well as the liquid residue. No significant nmr spectral difference between degraded and undegraded oil was observed even in those cases where there were visual evidences of physical change (viscosity and color).

The implications of these findings are that (a) no significant change in the chemical environment around the carbon or fluorine occurs in the degradation process, or (b) the concentration of such chemically changed species is so low that they escape detection by nmr, or (c) the degradation products are volatile and are not being collected with the distillate, or finally (d) the degradation products are short lived species and recom-

bine before nmr spectra can be obtained. Experiments described below were designed to exclude some of these possibilities.

Table I presents representative examples of experimental conditions for the lubricant degradation that culminated in the nmr result. The differences in appearance of the titanium coupons noted in the last column suggested the desirability of surface X-ray diffraction measurements to identify the composition of the corrosion products. Dr. Charles H. Pitt, a professor of metallurgy, assisted us with the necessary measurements on a Philips Diffractometer. All coupons were examined under copper  $K_{\alpha}$  X-radiation ( $\lambda \approx 1.54 \text{ \AA}$ ).  $\text{TiOF}_2$ ,  $\text{TiF}_3$ , and traces of  $\text{TiO}_2$  were detected on the metal surfaces.

In addition, a white powder was deposited on the walls of the glassware. Scrapings of this residue were also tested and found to be composed of fluorides of titanium,  $\text{TiF}_3$  and possibly  $\text{TiF}_4$ . The oxides and oxyfluorides of titanium were present only when the injected gas was either air or pure oxygen. A possible conclusion to be drawn from the presence of titanium fluorides is that the degradation of PR-143 involves the generation of reactive fluorine either as fluoro-organic free radicals or as a free fluorine radical. This agrees with the mechanism presented by Gumprecht at the 1968 Gordon Fluorine Conference,<sup>2</sup> the results of an earlier study by Sianesi et al.,<sup>3</sup> and the data of Snyder and Dolle.<sup>4</sup>

The proposed mechanism of oxidative degradation (in the absence of metals) is a free radical process with initiation followed by a  $\beta$ -scission propagation step. In the polymer, the C-C bond is the weakest, and destruction of this bond causes the whole molecule to decompose with the

Table I. Representative experimental conditions for degradation of DuPont PR-143 light engine lubricant subsequently examined by  $^{13}\text{C}$  and  $^{19}\text{F}$  nuclear magnetic resonance spectroscopy.

TEMPERATURE =  $316^\circ\text{C}$  ( $600^\circ\text{F}$ )

<u>Heating Time</u>	<u>Injected Gas</u>	<u>Gas Flow Rate</u>	<u>Pressure on System</u>	<u>Metal Coupon</u>	<u>Final Metal Appearance</u>
72 hrs	Air	80 ml/min	Atm.	Ti	violet
24 hrs	$\text{N}_2$	80 ml/min	Atm.	Ti	maroon
24 hrs	$\text{O}_2$	80 ml/min	Atm.	Ti	dull gray
24 hrs	dry air	80 ml/min	Atm.	Ti 6Al 4V Alloy	dull gray
6 hrs	$\text{N}_2$	80 ml/min	180-190† mm Hg	Ti	maroon*
6 hrs	$\text{O}_2$	80 ml/min	180-190† mm Hg	Ti	dull gray*
10 hrs	none	-	60 $\mu\text{m}$ Hg	V	brown-black
4 hrs	He	80 ml/min	150 $\mu\text{m}$ Hg	V	black <sup>§</sup>
4 hrs	$\text{O}_2$	80 ml/min	150 $\mu\text{m}$ Hg	V	black <sup>+</sup>

<sup>†</sup>Degradation sped up dramatically at low gas pressures.

\*Corrosion was less pronounced on that portion of the coupon swept continuously by injected gas.

<sup>δ</sup>A powdery dark green precipitate was noted in the residue.

<sup>+</sup>A powdery yellow-green precipitate appeared in the residue.

evolution of corrosive gaseous products. If the mechanism as proposed is correct, then the degradation products should contain components which hydrolyze to strong acids. This we confirm by a potentiometric titration of the water soluble components of the lubricant "distillate" using KOH titrant. This procedure yielded a multistep titration curve indicating the free acid generated was not simply HF but rather the hydrolysis products of perfluoroacetyl fluoride, a predicted decomposition product.

Since the proposed degradation mechanism involves free radicals, we carried out electron spin resonance experiments on the departmental Varian V-4502 spectrometer. A sample cell was fashioned from 4 mm O.D. Pyrex tubing. Metal filings were inserted with the PR-143 lubricant, and the cell was evacuated. A great deal of outgassing from the surface of metal filings was noted. The cell was then sealed under vacuum. The spectrometer is equipped to maintain a sample at a temperature of 250°. As the sample was heated, outgassing resumed, and the esr spectrometer became untunable.

Fluorine is not the effluent gas. This was verified by its unreactivity with lithium metal over a twelve hour period. The gas is probably one of the lighter organic fractions resulting from the degradation of the lubricant. Even if we had succeeded in overcoming outgassing problems, trace amounts of free radicals inevitably present in the heated lubricant could give detectable esr signals unrelated to the main degradation pathway. Since these signals may not necessarily lie in the same field region as those corresponding to paramagnetic degradation products or intermediates or may be so weak as to be effectively masked, the situation is by no means

hopeless. However, we did not have sufficient manpower to pursue these esr experiments further and still carry out experiments described below that were more rapidly fruitful.

Since a variety of components is produced by the proposed degradation mechanism, analysis by gas chromatography was indicated. A Hewlett-Packard 700 gas chromatograph with a thermal conductivity detector and a 240 temperature programmer was then used to examine the distillate in a Freon solvent,  $\text{CCl}_2\text{FCF}_2\text{Cl}$ . A three foot UC-98 copper column was employed in these experiments. There were light fractions detected in all samples including the untreated lubricant. The percentage of light fractions increased markedly with visually detectable degradation of the lubricant. Chromatographic peak shapes suggested that the degradation products are homologues of varying chain length, as expected from mechanistic arguments.

Mass spectral analysis was carried out by electron impact ionization using the mass spectrometer as a gas chromatograph detector. The components isolated with this technique are fully supportive of the proposed mechanism, with those degradation products predicted,<sup>3</sup> such as perfluoroacetyl fluoride,  $\text{C}_3\text{F}_6$ , and  $\text{COF}_2$ , actually observed.

Quantitative thermogravimetric (TGA) kinetic studies of the degradation of PR-143 lubricant are now essentially complete. An analysis by Fuoss et al.<sup>5</sup> has been used to determine activation energies and Arrhenius statistical factors from the inflection point of TGA curves. Our results are similar to those reported by Fuoss et al. for the degradation of Teflon and polystyrene. This kinetic TGA analysis is being prepared for publication.

Analysis of the lubricant degradation kinetics by TGA with metals present

does not appear promising because of the simultaneous corrosion of the metal catalyst and its concurrent weight gain.

In summary, a variety of experimental tools have been used in this laboratory to confirm a free radical mechanism for the degradation of a polyperfluoroalkylether. Thermogravimetric kinetic studies have yielded new information regarding the activation energy associated with the thermal degradation of the polymer.

References:

1. W. H. Gumprecht, "PR-143: A New Class of High Temperature Fluids," ASLE Trans. 9, 24-30 (1966), see the discussion immediately following this paper.
2. W. H. Gumprecht, private communication.
3. D. Sianesi, V. Zamboni, R. Fontanelli, and M. Binaghi, "Perfluoropolyethers: Their Physical Properties and Behaviour at High and Low Temperatures," Wear, 18, 85-100 (1971).
4. C. E. Snyder, Jr. and R. E. Dolle, Jr., "Development of Polyperfluoroalkylethers as High Temperature Lubricants and Hydraulic Fluids," ASLE Trans., 19, 171-180 (1976).
5. R. M. Fuoss, I. O. Salyer, and H. S. Wilson, "Evaluation of Rate Constants from Thermogravimetric Data," J. Polymer Sci., 24, 3147-3151 (1964).

APPENDIX II:

Description of Photoacoustic Spectroscopy Experiments  
Carried Out at Utah Under AFOSR Sponsorship as Described  
at the 173rd National American Chemical Society Meeting  
in New Orleans, March 22, 1977.

PHOTOACOUSTIC SPECTROSCOPY OF NEODYMIUM (III) GLASS.

Michael M. Farrow, Max Auzanneau, Roger K. Burnham,  
Neil Purdie, and Edward M. Eyring, Departments of  
Chemistry, University of Utah, Salt Lake City, Utah  
84112 and Oklahoma State University, Stillwater, Okla-  
homa 74074.

ABSTRACT

Photoacoustic spectroscopy has been used to measure the visible absorption spectrum of neodymium (III) laser glass. The experimental arrangement consisted of an argon ion pumped, cw, 30 mw, rhodamine 6G dye laser, a 400 Hz beam chopper, a sample with a ceramic piezoelectric transducer attached, and a lock-in amplifier. It was shown experimentally that the onset of fluorescence substantially lowers the acoustic signal and alters the acoustic phase angle. A correlation between lifetime of the excited state and acoustic phase angle is observed. Applications of photoacoustic spectroscopy to rapid heterogeneous reaction kinetics are also considered.

There has been a recent revival of interest in photoacoustic spectroscopy or PAS as an analytical tool for obtaining the electromagnetic spectrum of opaque materials. Many of the recent publications on this subject have come from Bell Laboratories which is appropriate since Alexander Graham Bell<sup>1</sup> first reported the photoacoustic effect in 1881. Those who are unfamiliar with the technique may be interested in perusing one of the recent review articles<sup>2,3</sup> on PAS.

There are several features of the most recent<sup>2</sup> of these review articles that have a bearing on the present talk. As noted in the textual material, PAS of solids typically involves the irradiation of a surface in an enclosed, gas-filled cell by a chopped beam of light. If the wavelength of the monochromatic, periodic light beam entering the cell through a transparent window is one that the sample surface absorbs, the subsequent thermal deexcitation of the energy states excited by the light beam will give rise to pressure oscillations in the surrounding gas that are proportional to the absorption of the light by the surface. These oscillations are detectable with a microphone also located in the cell, and the resulting signal is amplified and measured by a lock-in amplifier.

Figure 1 of reference 2 is the PAS spectrum of a solid lanthanide oxide and Figure 2 indicates that better spectral resolution in microphonic PAS is achieved at a higher chopping frequency of the incident light beam.

McClelland and Kniseley<sup>4</sup> provide a schematic of a typical microphone PAS cell and also a plot of experimental data that suggests there is very little to be gained in Signal to Noise and nothing to be gained in photo-acoustic signal by working at chopping frequencies exceeding about 50 Hz.

In a subsequent note<sup>5</sup> these same authors provide a somewhat clearer schematic view of how a microphone type PAS cell works and how one can overcome the disadvantage of light scattering from the sample on to the microphone by relocating the latter at the end of an interconnecting air duct.

The next slide is a photograph of a prototype commercial photoacoustic spectrometer that I saw last month in the laboratory of Dr. Gordon Kirkbright

at the Imperial College in London, England. The OAS label stands for "Opto-Acoustic Spectrometer" which is the terminology some prefer for the PAS technique. Such an instrument combines ordinary uv-visible transmission spectroscopic capability with PAS capability. Some persons in the analytical instrument industry foresee a multimillion dollar per year business in photoacoustic spectrometers.

Rosecwaig<sup>3</sup> has demonstrated the feasibility of identifying fluorescent lines in a PAS spectrum. In the upper trace of his Figure 12 Rosencwaig has shown the PAS spectrum of a solid sample of holmium(III) oxide to which a fluorescence quenching impurity has been added. In the same Figure 12, in the lower PAS spectrum of pure, solid holmium(III) oxide many lines are missing because of the de-excitation of the corresponding levels by fluorescence.

Hordvik<sup>6</sup> has used a piezoelectric transducer as the detector in his PAS determinations of optical absorption coefficients of highly transparent solid materials utilized in his infrared laser work. On the next slide (Figure 1 of reference 6) we see a schematic of Hordvik's apparatus for making such measurements. Hordvik's use of a piezoelectric detector operated in the 150 to 3000 Hz chopping frequency range does not capitalize on one of the principal potential advantages of such a transducer over a microphone. Since a piezoelectric transducer can be operated at frequencies as high as hundreds of megahertz (frequencies far beyond the upper limit accessible to microphones), there is, in principle, no reason why a piezoelectric detector cannot be used in PAS experiments to detect very rapid transient phenomena such as fluorescence. We may expect with

such a transducer that the upper frequency limit will be imposed by the lock-in amplifier.

Other potential advantages of a piezoelectric transducer are the possibility of improved coupling between an irradiated sample surface and detector with a consequent enhanced signal to noise ratio and easier analysis of the phase relationship of incident chopped light to the detected sound wave.

In the investigations reported here we have used barium titanate piezoelectric transducers in a prototype PAS spectrometer shown schematically in Figure 1. [This and all subsequent figures are found at the end of this Appendix.] In Figure 2 we show a PAS absorption spectrum of a powdered  $\text{Nd}_2\text{O}_3$  sample attached to a front surface mirror with Eastman 910 cyanoacrylic adhesive. In this case the barium titanate transducer attached to the back of the mirror was an Edo-Western Corp. EC-64 with a resonant frequency of  $\sim 45\text{kHz}$ . The light source was a 500 watt high pressure xenon arc lamp passed through a monochromator with f/1 optics and a 10 to 20 nm bandpass. The spectra have been source compensated, i.e. normalized for differences in lamp intensity at different wavelengths. The signal was received with a Princeton Applied Research Model 184 charge amplifier and Model 124 lock-in amplifier. The light beam was chopped mechanically at a frequency of 135 Hz and the output signal level was in the range of 100 to 200  $\mu\text{V}$ . The point of primary interest to Figure 2 is that it is almost trivially easy to obtain the highly detailed visible light absorbance spectrum of neodymium(III) from a completely opaque solid sample using the above described PAS spectrometer.

In Figure 3 we have compared the PAS spectrum of an essentially transparent neodymium(III) glass laser rod (Owens-Illinois) with the absorbance spectrum of the same material obtained with a Beckman DB LSI-II microcomputer. The PAS experiment was performed with the laser glass (~2cm thick) mounted on a first surface mirror backed by a barium transducer as in the experiment of Figure 2. All other features of the experiment were as described above. The 10 to 20 nm bandpass of the monochromator was imposed by arc wander in the light source (that had been minimized by a permanent magnet).

In Figure 4 an argon ion laser pumped rhodamine 6G dye laser (Spectra Physics) beam chopped mechanically at 500Hz illuminated a sample of neodymium(III) laser glass. The barium titanate transducer was mounted on an aluminum metal saddle on the barrel of the Nd:glass rod so that the incident chopped beam passed parallel to and within ~1cm of the transducer. A 0° phase angle means that the acoustic signal arrives with no time delay from the excited material in the sample. In curve a of Figure 4 the chopped laser beam was focused to a ~ 10 $\mu$ m diameter spot on the laser rod whereas for curve b the unfocused dye laser beam had a ~ 2cm diameter on the Nd:glass. Curve a goes negative because the acoustic signal is delayed as the ground electronic state population of neodymium(III) ions in the laser glass is depleted by the intense ( $6 \times 10^6$  watts/cm<sup>2</sup>) dye laser beam. The acoustic signal occurs only as the metastable fluorescent state emits photons and returns to the ground state since the acoustic signal arises only during the radiationless decay

of higher excited electronic states to the metastable state of the neodymium(III) ions. Engstrom et al.<sup>7</sup> have indicated the calculations that could be used to determine the lifetime of a fluorescent state from this type of PAS phase angle data. The neodymium(III) fluorescence lifetime of the order of 0.5 msec is, of course, already well known, but this experiment confirms the feasibility of comparing fluorescence lifetimes for a given ion or molecule under a variety of physical conditions (e.g., dissolved, adsorbed, vaporized, or in a glass like matrix) using PAS phase angle information.

The results of our most recent experiment are shown in Figure 5. As in the case of Figure 3, a PAS study of Nd laser glass was undertaken by sticking a piece of laser glass to a front surface mirror with a barium titanate transducer stuck to the back of the mirror. An acousto-optically (Debye-Sears) modulated (to 100% depth) 514.5 nm beam from a ~100 milliwatt CW argon ion laser illuminated the front face of the Nd:glass laser rod. The heavy black line of Figure 5 is the PAS signal strength (measured in microvolts) over a range of chopping (modulation) frequencies of the incident green light extending from 100Hz to 206 KHz. The measured PAS signal was stable at all frequencies and was definitely attributable to the incident optical beam since the signal went to zero when the argon ion laser beam was blocked. Thus it is clear that when a piezoelectric transducer is attached to a solid sample there is essentially no upper limit to the modulation frequency for use in PAS other than that imposed by the method of light beam modulation or the frequency range accessed by the lock-in amplifier. This contrasts with the microphonic PAS approach

that is limited to much lower chopping frequencies. It is also clear from Figure 5 that signal strength will be greatest when the modulation frequency of the incident light beam is near the resonant frequency of the piezoelectric transducer. In other words, Figure 5 assures us that we have a powerful kinetic spectroscopic tool for studying comparatively fast reactions occurring on opaque surfaces.

Looking ahead, we foresee several ways of applying the piezoelectric transducer PAS to unique advantage. For instance, a continuing problem with high power Nd:glass laser systems is damage to the glass laser rods caused typically by back reflections from the target or other surfaces. In principle, two or more piezoelectric transducers on the barrel of a laser rod would permit the location by PAS of damage centers before they became large enough to detect with the naked eye.

In a more chemical vein, it will be possible to determine nanosecond time scale fluorescence lifetimes of molecules adsorbed on opaque surfaces and compare their PAS determined fluorescence lifetimes in the adsorbed state with lifetimes determined by flash photolysis for the same fluorescing molecules in bulk solution or in the gas phase. The frequency response of our present lock-in amplifier of ~250 kilohertz would limit directly measurable fluorescence lifetimes to those longer than about 20 nanoseconds. However, with more sophisticated receiver techniques we foresee the possibility of making measurements down to 20 picoseconds.

Our initial and continuing principal interest in the PAS technique is as a kinetic tool for studying the rate and mechanism of corrosion at high temperatures of a metal surface by various fluids. With the surface

of interest evaporated onto a piezoelectric transducer and its exposed surface bathed in a corrosive fluid one has an experimental configuration quite unsuited to the use of a microphone detector. A microphone would not relay PAS information from the solid surface of interest. Furthermore, the piezoelectric transducer is physically much less vulnerable to damage in such a hostile environment than is the microphone.

References:

1. A. G. Bell, "Upon the Production of Sound by Radiant Energy," *Philos. Mag.*, 11, 510-528 (1881).
2. D. M. Munroe and H. S. Reichard, "Practical Photoacoustic Spectroscopy of Solids," *American Laboratory*, February, 1977, p. 119.
3. A. Rosencwaig, "Photoacoustic Spectroscopy, A New Tool for Investigation of Solids," *Anal. Chem.*, 47, 592A (1975).
4. J. F. McClelland and R. N. Kniseley, "Photoacoustic Spectroscopy with Condensed Samples," *Appl. Optics*, 15, 2658 (1976).
5. J. F. McClelland and R. N. Kniseley, "Scattered Light Effects in Photoacoustic Spectroscopy," *Appl. Optics*, 15, 2967 (1976).
6. A. Hordvik and H. Schlossbert, "Photoacoustic Technique for Determining Optical Absorption Coefficients in Solids," *Appl. Optics*, 16, 101 (1977).
7. H. Engstrom and L. F. Mollenauer, "Chronospectroscopy of Exchange - Coupled Cr<sup>3+</sup>-Ion Pairs in Ruby," *Phys. Rev. B*, 7, 1616 (1973).

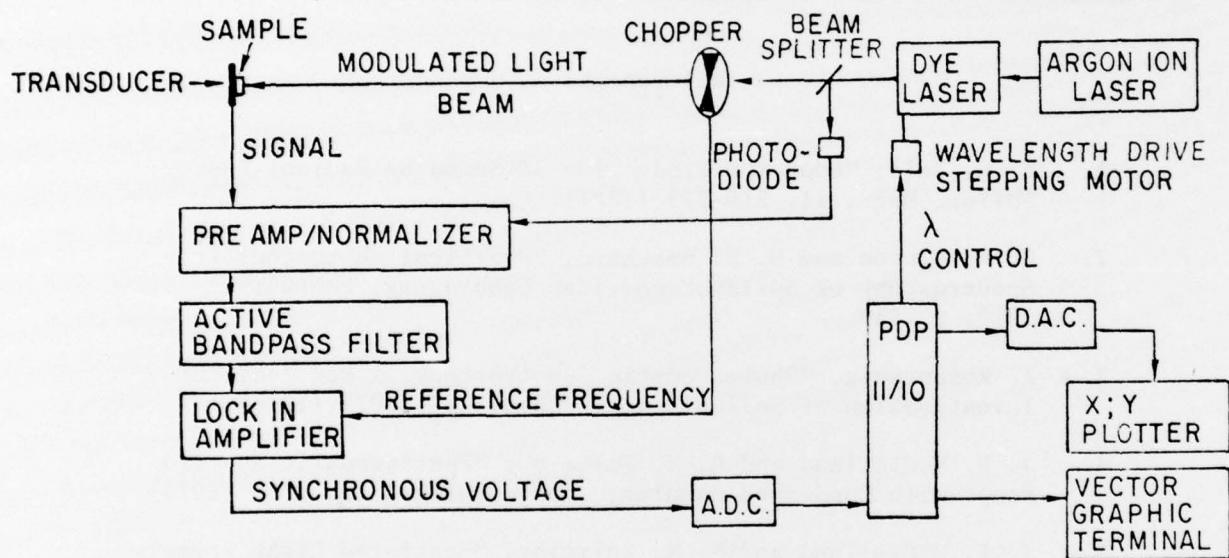


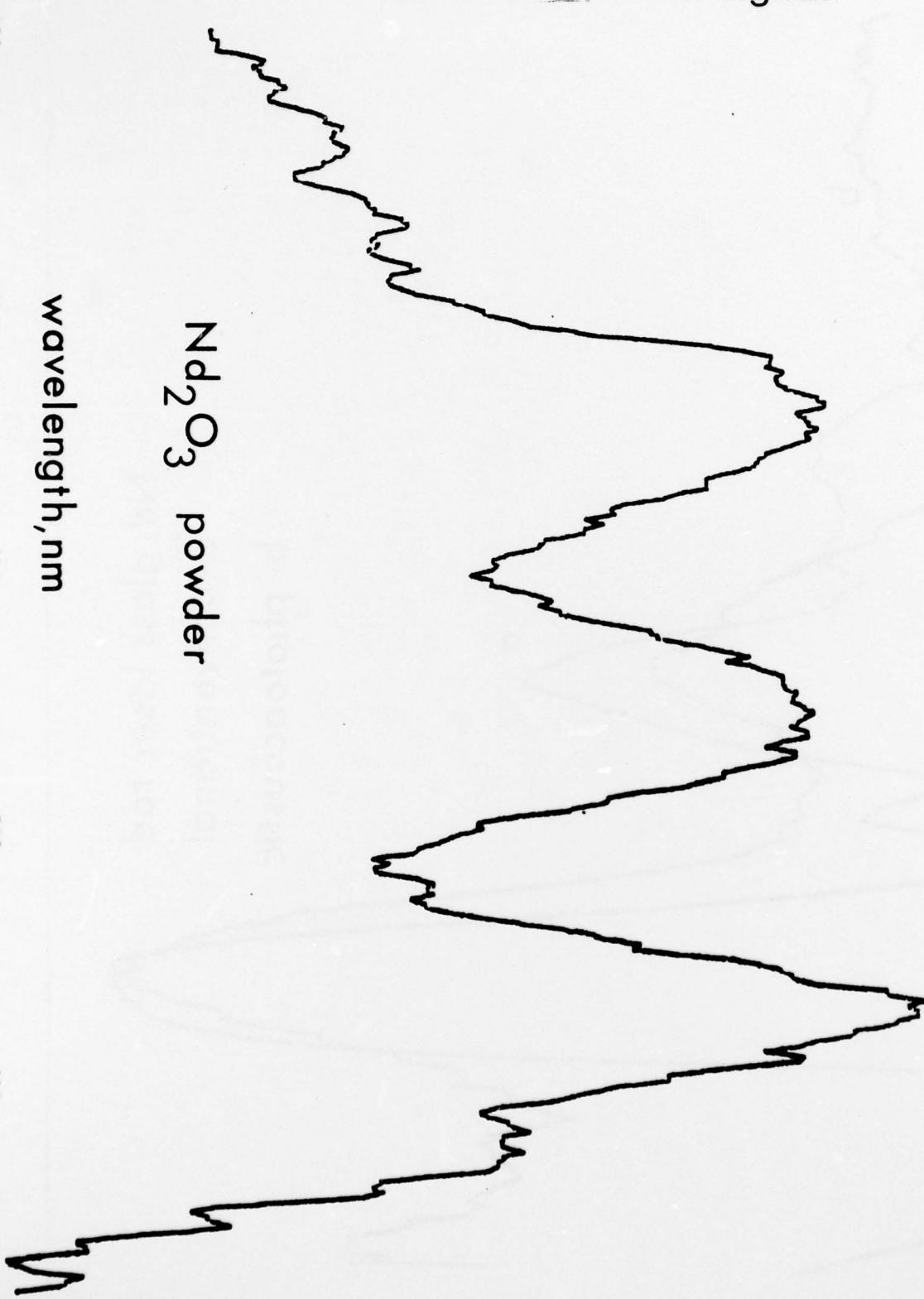
Fig. 1. Schematic of experimental apparatus. Argon ion laser is Spectra Physics model 165 operating with broadband mirror at up to 3 watts cw. Dye laser is Spectra Physics model 365 using Rhodamine 6 G dye and operating at up to 500 mw cw. Preamp and active band pass filter are of local manufacture and supply 10 db of gain. Lock-in is an Ithaco model 195 supplying 60 db of gain and operating with a filter constant of 1.25 sec.

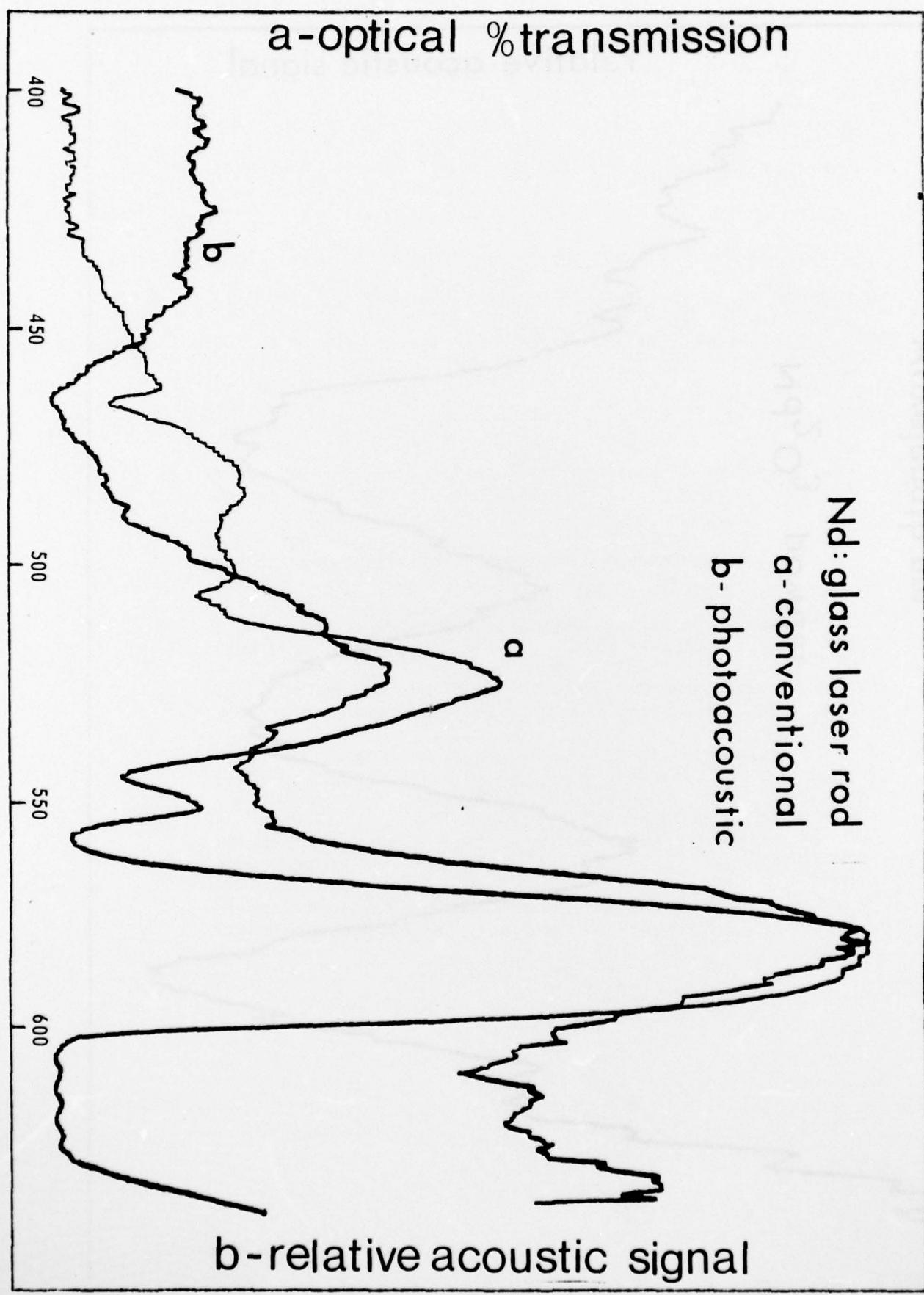
relative acoustic signal

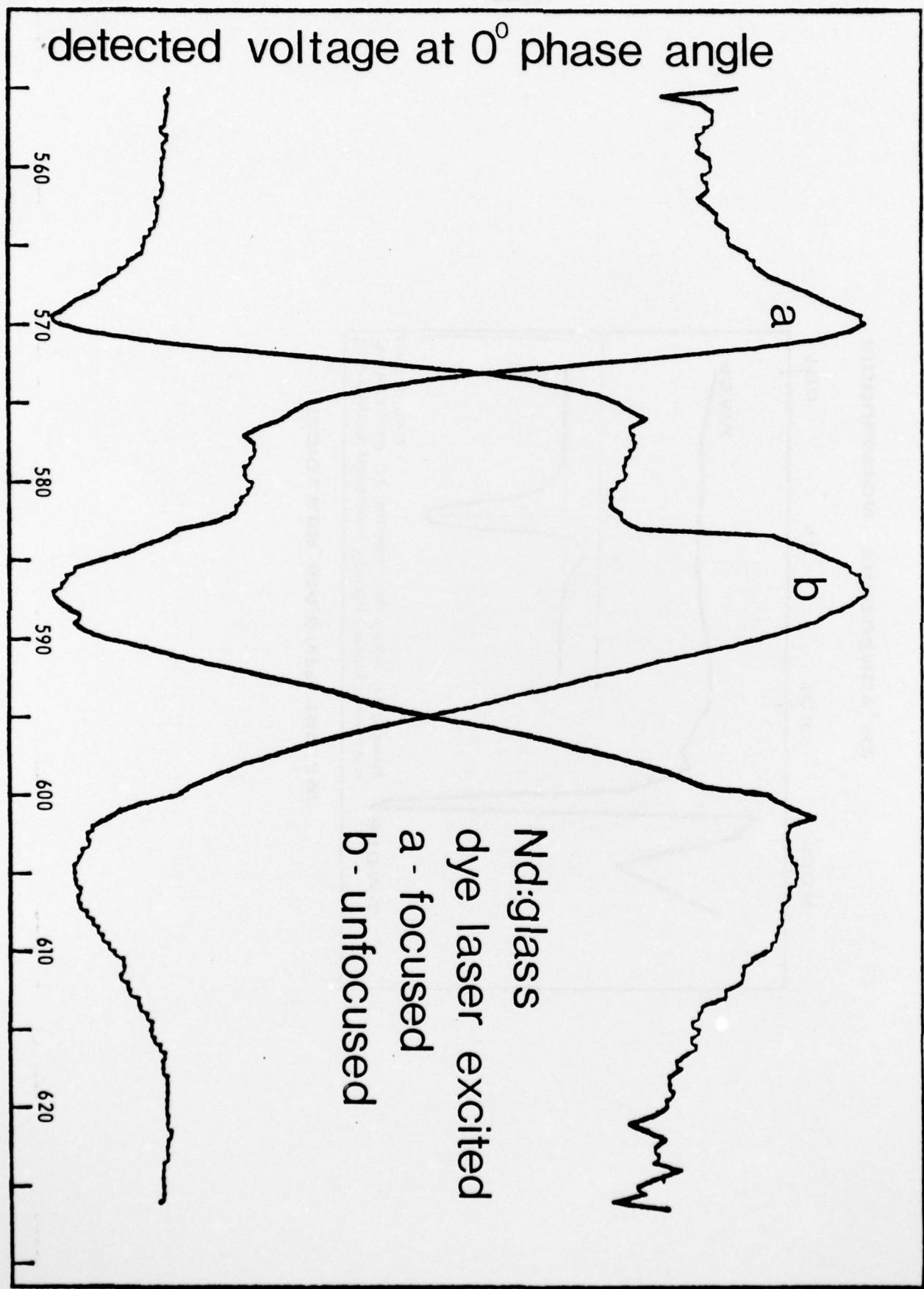
Nd<sub>2</sub>O<sub>3</sub> powder

400  
450  
500

550  
600

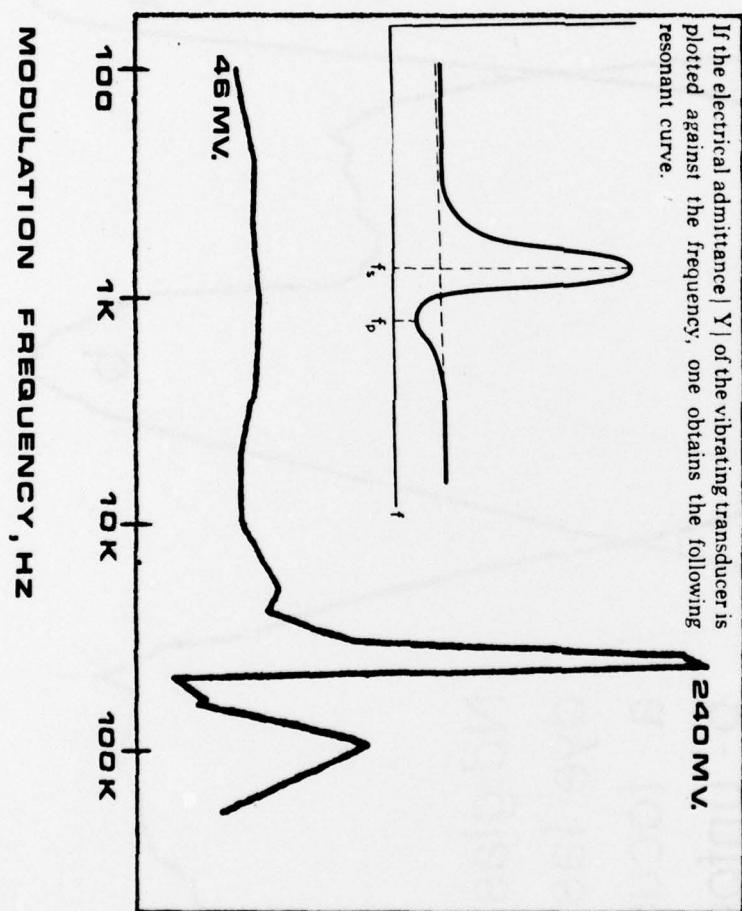






ND:GLASS, 514.5 NM; 100 MW

If the electrical admittance  $|Y|$  of the vibrating transducer is plotted against the frequency, one obtains the following resonant curve.



SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR - TR - 77 - 6649	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) RATES OF RAPID CHEMICAL REACTIONS	5. TYPE OF REPORT & PERIOD COVERED FINAL rept. Dec 1972 - Jan 31 1977	
6. AUTHOR(s) Edward M. Eyring	7. CONTRACT OR GRANT NUMBER(s) AFOSR 76-2444-73	
8. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, University of Utah Salt Lake City, Utah 84112	9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2303/A2 61102F	
10. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research/NC Building 410, Bolling AFB, DC 20332	11. REPORT DATE March 28, 1977	
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES 29	
14. DISTRIBUTION STATEMENT (of this Report)	15. SECURITY CLASS. (of this report) Unclassified	
Approved for public release; distribution unlimited.	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	D D C REF ID: A651147 JUN 8 1977 A -	
17. SUPPLEMENTARY NOTES		
18. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
kinetics carbocyanine dyes silver (I) thiosulfate complexation kinetics crown ethers	minicomputerization laser Debye-Sears ultrasonic absorption titanium metal fluorescence	electric field jump polyperfluoroalkyl ether photoacoustic spectroscopy corrosion
19. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
The kinetic behavior of carbocyanine dyes in low temperature glasses was investigated by a laser flash photolytic technique. Ultrasonic absorption kinetic studies of the complexation of silver (I) ion by thiosulfate anion and of many other cations by several ligands including particularly crown ethers have also been completed.		
The minicomputerization of a laser Debye-Sears ultrasonic absorption technique proved especially fruitful and led to a similar digitization of		

20. (continued) an electric field jump kinetic experiment.

An investigation of the thermal degradation of a polyperfluoroalkyl ether confirmed earlier conclusions regarding its free radical mechanism.

An unique photoacoustic spectroscopy experiment incorporating a piezoelectric transducer in place of a microphone was developed to study titanium metal corrosion. The technique also has potential interest for measuring fluorescence lifetimes of excited states in materials such as neodymium (III) oxide and neodymium laser glass.